

**ANALYSIS OF ELECTRICAL PROPERTIES OF THE P3HT-Bi<sub>2</sub>Te<sub>3</sub> INTERFACE FOR  
POLYMER-INORGANIC COMPOSITE MODELLING**

By

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A thesis submitted to Johns Hopkins University in conformity with the requirements for the  
degree of Master of Science in Engineering.

Baltimore, Maryland

May 2018

## ABSTRACT

Conductive polymer composite materials have attracted a lot of research attention due to the advantages they offer over inorganic conducting materials, including lower cost, ease of manufacturing, and lighter weight. Most research has been focused on dispersing inorganic nanoparticles throughout a polymer matrix to determine which combinations yield the best electrical properties. However, very little research has been done in this area at a macroscopic level, even though these studies at this level would be valuable in modeling the interactions between polymers and inorganic materials when combined in composites.

In this thesis, poly(3-hexylthiophene) and bismuth telluride were combined at a macroscopic level to develop an understanding of the electrical interactions between these two materials. A  $\text{Bi}_2\text{Te}_3$ -P3HT bilayer was combined in series with two segments of P3HT and used to determine if an interface resistance exists between the materials. The ideal resistance of this architecture was determined by estimating the sum of the resistance of each portion and assuming the current could pass between the P3HT and  $\text{Bi}_2\text{Te}_3$  without encountering an interface resistance. Then, the overall resistance of each device was measured and compared to this ideal resistance to determine whether an interfacial resistance was present, and if so, to what extent.

The results of this experiment showed that the measured resistance was substantially higher than the estimated ideal resistance of the devices. This result led to the conclusion that an interface resistance did, in fact, exist between the two materials used, and that the magnitude of this resistance is substantial. The data gathered from this experiment could prove useful for

future attempts to model the interactions of polymeric and inorganic materials in conductive composites.

Reader (Thesis advisor): Professor Howard E. Katz

## ACKNOWLEDGEMENTS

I would like to first thank my advisor, Professor Howard Katz. I had the privilege of learning how to conduct insightful research in his lab as well as taking a chemistry class that he taught, and I can say that he is a fantastic educator and expert in the field, as well as a positive role model for everyone working in his lab. This research endeavor would not have been possible without his guidance.

Also, thanks go out to the amazing researchers working in his lab, who I had the honor of working alongside during my time at Hopkins. There is not a better group of people to get to spend time around and learn from in a research environment. I must thank Dr. Hui Li, who taught me the procedures for fabricating devices and analyzing their properties. Also, thanks go to Jennifer Dailey for teaching me how to use much of the equipment I needed to use in the lab, and Jiyan Huang for many discussions about our experiments and results. Thanks also go out to Jeanine Majewski, who helped me keep my bearings straight during my time at Hopkins. Of course, I also thank Johns Hopkins for being such a great environment in which I could pursue my education and all the wonderful professors I had the pleasure of learning from.

I would especially like to thank my family for all the support they've given me throughout my time here. Thanks to my parents, who have continued to support me throughout my life and during my master's education. I would also like to thank my wife Elizabeth, who has been by my side through all the ups and downs of graduate school.

I couldn't have gotten here without all of you, and I can't thank you all enough.

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# INTRODUCTION

Conductive polymer composites present an appealing alternative to inorganic conducting materials for many applications <sup>[1]</sup>. They provide several advantages over metal conductors such as lighter weight, ease of processing and manufacturing, higher chemical resistance, and less exposure to toxic earth metals. Their use has been studied for a broad variety of applications such as light emitting diodes <sup>[2]</sup>, thermoelectric materials <sup>[3]</sup>, conductive adhesives <sup>[4]</sup>, and electromagnetic interference shielding <sup>[5]</sup>. Because of this, an extensive amount of research has been done on improving the electrical properties of polymeric composite materials, so they can become more viable alternatives to metals as conductors.

These materials were traditionally fabricated by adding a conductive filler to an insulative polymer matrix to produce a conductive composite of the materials <sup>[6]</sup>. The electrical properties of insulative polymers blended with conductive materials such as silver nanoparticles <sup>[7]</sup>, carbon black <sup>[8]</sup>, and other fillers have been studied for decades. Since the discovery of conductive polymers in 2000 <sup>[9]</sup>, research has been carried out on blending PEDOT:PSS, P3HT, PTH, and other conducting polymers with inorganic materials such as bismuth telluride or antimony telluride to improve the thermoelectric properties of these composite materials <sup>[10]</sup>.

Most research conducted in this area has been focused on functionalizing and dispersing nanoparticles throughout a polymer matrix and measuring the electrical and thermal properties of the resulting composite material. However, not much research has been performed on the properties of these materials when combined at a macroscopic level. Data gathered at this level could provide essential insight into the properties of the interface between these polymeric and inorganic materials, which would be necessary in the development of a comprehensive model for the interactions between the materials.

This would be highly beneficial in future research on improving the properties of these conductive composites.

To gain further insight into these interactions, the two materials poly(3-hexylthiophene) (P3HT) and bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) were combined so the electrical properties of the interface between the two materials could be studied more in depth. The P3HT was doped with 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) in amounts of 20%, 30%, and 40% by weight to improve its electrical conductivity. Macroscopic sized pieces of  $\text{Bi}_2\text{Te}_3$  were combined with F4TCNQ doped P3HT in a manner such that the devices mirrored the functionality of 2 resistors in series with a pair of parallel resistors. The device architecture is illustrated below in Figure 1. Using this architecture, the resistances of the bilayer devices could be compared to the resistances of the polymer and  $\text{Bi}_2\text{Te}_3$  segments of these devices. By doing so, it is possible to determine if an interfacial resistance exists between the two materials, and, if so, to what extent.

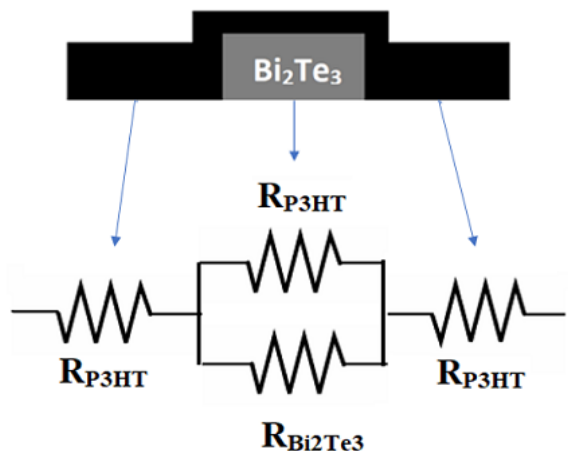


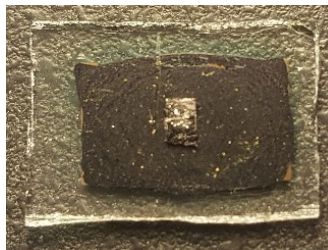
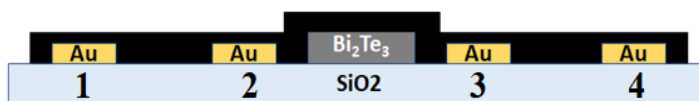
Figure 1. Segments of P3HT in series with  $\text{Bi}_2\text{Te}_3$ -P3HT bilayer, with circuit model.



## EXPERIMENTAL METHODS

Regioregular Poly(3-hexylthiophene) was purchased from Solaris (product SOL4106), and a 200 gram p-type bismuth telluride ingot was purchased from Thermoelectric Generator for use in this experiment. The P3HT was doped with F4TCNQ by a mixed solution method. First, the two were dissolved separately in chlorobenzene at a concentration of 5 mg mL<sup>-1</sup>. Each solution was heated and sonicated at 70°C for 30 minutes. The two solutions were then blended together to form doped polymer solutions that contained 20%, 30%, and 40% by weight of the dopant. These solutions were heated at 50°C and sonicated for 30 minutes to create the doped polymer solutions.

Gold electrodes were evaporated onto glass substrates with a channel length of 2.75 mm and a channel width of 5 mm. Novec 1700 was used to pattern the substrate by forming rectangular wells around 4 parallel electrodes. The substrate was cut along the patterning to form pieces that each contained 4 electrodes surrounded by the Novec coating. The bismuth telluride ingot was cut by hand to form pieces that were between 80  $\mu$ m and 180  $\mu$ m in thickness. The lengths of the pieces were between 1.67 mm and 1.81 mm, and the widths were between 2.35 mm and 2.66 mm. These Bi<sub>2</sub>Te<sub>3</sub> pieces were centered between the two center electrodes, and the doped polymer solution was drop cast over this configuration and left to dry overnight to form the devices. A diagram of the final device architecture can be seen below in Figure 2, along with an overhead image of a completed device. Before performing measurements, the devices were annealed at 120 °C for 10 min in a glovebox under nitrogen. This architecture was chosen so that measurements could be taken across the polymer film by measuring across electrodes 1 and 2 or electrodes 3 and 4. Taking measurements across electrodes 2 and 3 would then provide resistance values for the bilayer material.



*Figure 2. Diagram of device architecture along with numbered electrodes (left) and overhead view of completed device (right). The raised section in the middle is where polymer coats the  $\text{Bi}_2\text{Te}_3$  piece.*

Resistance measurements were made with the 4-probe method using an Agilent 4155C Semiconductor Parameter Analyzer. When measuring the resistances across the pieces of  $\text{Bi}_2\text{Te}_3$  coated in polymer, a digital Craftsman multimeter was used. The distances between the probes, widths and lengths of the films and  $\text{Bi}_2\text{Te}_3$  pieces, and film thickness measurements were made using a KEYENCE VK-X100 Laser Microscope. These measurements were all used in conjunction to calculate the apparent resistivity and apparent conductivity.

## RESULTS AND DISCUSSION

First, the resistances of the polymer film were taken and compared with resistance values taken across the bilayer material. The resistance measurements across the polymers films were carried out by placing the four probes equal distances apart with the current probes across electrodes 1 and 2 or across 3 and 4 and the voltage probes placed between the current probes. Measurements on the bilayer portions were carried out by placing the voltage probes across electrodes 2 and 3 and the current probes on electrodes 1 and 4. A side by side comparison of these measurement methods can be seen in Figure 3.

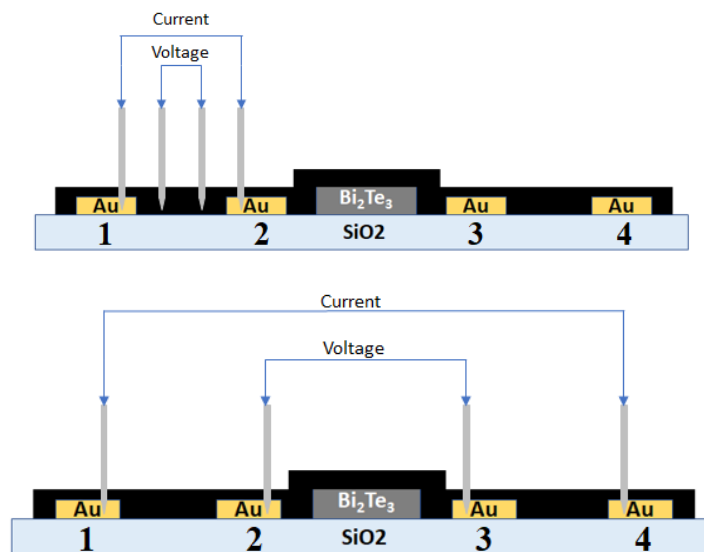


Figure 3. Resistance measurement method for polymer film (top) and bilayer material (bottom).

The apparent resistivity of each segment was calculated using the equation  $\rho = RA/L$ , where  $\rho$  is the electrical resistivity,  $R$  is the resistance,  $A$  is the cross-sectional area of the devices and films, and  $L$  is the distance between the voltage probes. Apparent resistivity is given in units of  $\Omega \text{ cm}$ . For the polymer film measurements, the puncture holes left by the probes were determined to be 0.183 cm apart by laser microscope, so this value was used for  $L$  when performing the calculations. Since the voltage probes were placed across the center two electrodes for the bilayer measurements, the channel length of 0.275 cm was used for  $L$ . The cross-sectional area was obtained by multiplying the device widths by the thickness measurements, both obtained by laser microscope. Apparent conductivity was calculated by taking the inverse of the apparent resistivity and is given in units of  $\text{S cm}^{-1}$ . The values for resistance, apparent resistivity, and apparent conductivity can be seen in Table 1.

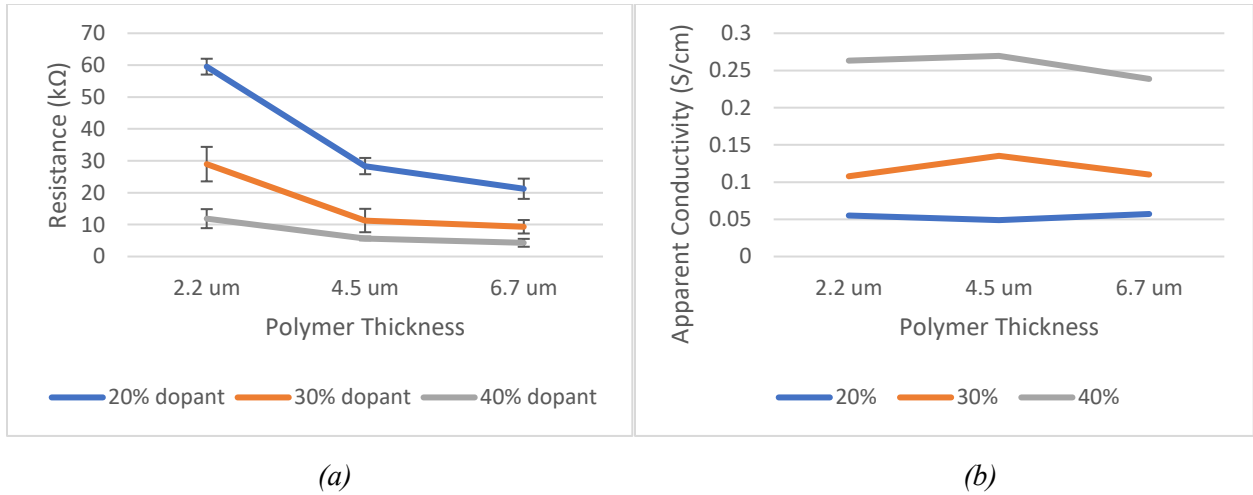
Device/Dopant Conc.	Resistance (k $\Omega$ )	Apparent Resistivity ( $\Omega$ cm)	Apparent Conductivity (S cm <sup>-1</sup> )
Polymer/20%	25.1 $\pm$ 6.3	17.56	0.057
Polymer/30%	8.4 $\pm$ 2.1	5.88	0.170
Polymer/40%	4.5 $\pm$ 1.2	3.15	0.317
Bilayer/20%	50.5 $\pm$ 7.8	23.51	0.042
Bilayer/30%	22 $\pm$ 3.2	10.24	0.097
Bilayer/40%	12 $\pm$ 2.1	5.59	0.179

*Table 1. Resistances, apparent resistivities, and apparent conductivities of polymer films and bilayer devices. Each row contains data from 5 devices.*

For each level of dopant concentration, the apparent conductivities of the bilayer portions of the devices came out to slightly more than half those of the polymer portions. This contradicted the expectation that the addition of Bi<sub>2</sub>Te<sub>3</sub>, which has been reported to have conductivity values as high as  $1.5 \times 10^3$  S cm<sup>-1</sup> [11][12], to the film would increase the apparent conductivity of the device by providing a more conductive pathway for the electrical current. Resistive measurements performed on the Bi<sub>2</sub>Te<sub>3</sub> ingot, with a height of 5.08 cm and a cross-sectional diameter of 2.54 cm, came out to 1-3  $\Omega$  with the probes placed 1 mm apart across the cross-sectional surface. If P3HT and Bi<sub>2</sub>Te<sub>3</sub> have any sort of compatibility, and if electrical current can pass relatively freely between these two materials, then the apparent conductivity would certainly be expected to increase from the addition of bismuth telluride to the polymer. This raised the question of whether the increase in apparent resistivity was due to a weak contact at the interface between the polymer and Bi<sub>2</sub>Te<sub>3</sub>, or if the increase was due to an interfacial resistance that exists between the two materials.

This question was tested by fabricating a new batch of devices where polymer solution was drop cast on top of the Bi<sub>2</sub>Te<sub>3</sub> pieces and electrodes to form films that were measured to be 2.2  $\mu$ m, 4.5  $\mu$ m, and 6.7  $\mu$ m in thickness. Again, dopant concentrations of 20%, 30%, and 40% were used to ensure that

the behavior observed was consistent at different concentrations. Resistance measurements were made across the bilayer portions of these devices by placing the voltage probes across electrodes 2 and 3 and the current probes across electrodes 1 and 4, like in the bottom graphic in Figure 3. These measured resistance values were converted to apparent conductivity. These apparent conductivity calculations were compared to determine if the measured values would increase as the amount of polymer increased, which would indicate that the decrease in apparent conductivity seen earlier was due to a weak interfacial contact between the materials. Charts displaying the measured values for resistance and apparent conductivity can be seen below in Figure 4. Each resistance value is the average of measurements taken from 4 devices.



*Figure 4. Comparison of resistance and apparent conductivity in bilayers with various polymer thicknesses. Resistances are shown in (a) and apparent conductivity can be seen in (b).*

The measured values for resistance decrease by roughly 50% when the thickness is increased from 2.2 μm to 4.5 μm and by about 33% when the thickness is increased from 4.5 μm to 6.7 μm. This pattern is consistent at each level of dopant concentration. However, the apparent conductivity of the

devices stayed relatively constant across the different levels of device thickness. These results suggest that the apparent conductivity difference between the previous polymer and bilayer measurements was not due to an insufficient amount of polymer contacting the bismuth telluride, and was, in fact, due to an interfacial resistance between the two materials.

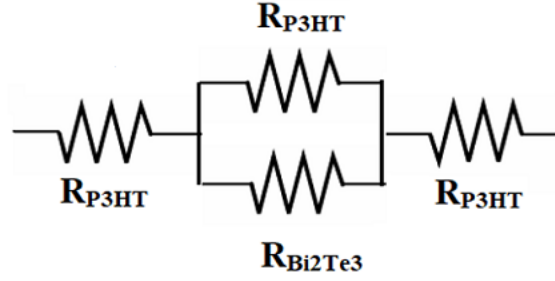
To determine the magnitude of this interfacial resistance, the resistances of the polymer portion and the bismuth telluride with polymer coating portion needed to be calculated to estimate each of their individual contributions to the overall bilayer resistance. The devices used to perform the first measurements, shown in Table 1, had additional gold electrodes evaporated on top of the polymer portion of the devices and on top of the bismuth telluride pieces coated in P3HT. These electrodes were 50 nm in thickness, with a channel length of 0.025 cm. The polymer portions were measured using the 4-probe method, with the voltage probes placed on these new electrodes. Measurements on the  $\text{Bi}_2\text{Te}_3$  bilayers were performed using the handheld multimeter, with the one probe placed on each electrode on top of the bilayer. The apparent resistivity values shown in Table 1 were cross referenced across these new calculations for consistency, and the apparent resistivity across the  $\text{Bi}_2\text{Te}_3$  coated in P3HT was determined. Apparent resistivity values are shown in Table 2. Each value was obtained by taking resistance measurements on 3 different devices, converting to apparent resistivity, and averaging those values together.

Dopant Conc.	Apparent Polymer Resistivity	Apparent $\text{Bi}_2\text{Te}_3$ Resistivity
20%	18.70	0.206
30%	7.58	0.154
40%	3.91	0.119

*Table 2. Apparent resistivity measured across polymer and bismuth telluride coated with P3HT.*

The values calculated for the apparent polymer resistivity were very close to the originally calculated values. Apparent resistivities for the  $\text{Bi}_2\text{Te}_3$  pieces coated with P3HT were much lower than those of just the polymers, though the measured resistances were somewhat higher than values measured for  $\text{Bi}_2\text{Te}_3$  alone. This would stand to reason due to the measurement method, where the probes were placed on the polymer film coating the  $\text{Bi}_2\text{Te}_3$ . The current produced by the measurement probes travelled out of one probe, through the polymer film, into the  $\text{Bi}_2\text{Te}_3$ , through the film again, and into the other probe. Therefore, the polymer film contributed to the overall resistance, causing the probe measurements to give larger resistance values than those gathered from pure  $\text{Bi}_2\text{Te}_3$ . This also explains why the apparent resistivity decreases with increasing dopant concentration.

With the apparent resistivities of both the polymer and the  $\text{Bi}_2\text{Te}_3$  coated in polymer, the resistance contribution of each to the bilayer devices could be estimated. The length, width, and thickness of each portion of the bilayer devices reported in Table 1 were used along with the apparent resistivity values in Table 2 to estimate the resistance of each portion, using the equation  $R = \rho L/A$ . The length of the  $\text{Bi}_2\text{Te}_3$  bilayer segments was measured using the laser microscope. Then, as the voltage probes were placed on electrodes 2 and 3, and that distance between those was measured to be 0.275 cm, the length of the polymer film between the probes and the  $\text{Bi}_2\text{Te}_3$  pieces was calculated by subtracting the width of each piece from 0.275. If no interfacial resistance were present between the polymer and  $\text{Bi}_2\text{Te}_3$ , and if the devices followed the circuit model shown in Figure 1, then the sum of these estimated resistances would be expected to be approximately equal to the measured values of the resistances across the bilayer devices shown in Table 1. Calculated values for resistances of each portion of the bilayers are shown in Figure 7, along with the calculated and measured total resistances of the bilayers.



Dopant Conc.	Measured $R_{Total}$ ( $\Omega$ )	$R_{P3HT}$ ( $\Omega$ )	$R_{Bi2Te3+P3HT}$ ( $\Omega$ )	Calculated $R_{Tot}$ ( $\Omega$ )
20%	50,500	10,837.5	16	21,696
30%	22,000	5,189	13	10,391
40%	12,000	2,945	10	5,900

Figure 5. Equivalent circuit model and calculated values for  $R_{P3HT}$  and  $R_{Bi2Te3+P3HT}$

The results show that, for each level of dopant concentration, the calculated total resistance contributions of the polymer and  $Bi_2Te_3$  come out to approximately half of the measured total resistance of the bilayer devices. If the current were able to enter the  $Bi_2Te_3$  effectively, therefore following the  $R_{Bi2Te3}$  resistive pathway in the equivalent circuit, then the total resistance would be expected to be much closer to the calculated value, and certainly lower than the resistance of the polymer film by itself. The much higher resistance measured for the bilayer devices suggests a couple of possibilities. Either the current is following the polymer film coating the  $Bi_2Te_3$ , which would have a higher resistance due to various imperfections in the film, or the current is entering the  $Bi_2Te_3$ , but experiencing a high interfacial resistance that increases the total resistance measured substantially. In either case, the results seem to suggest the presence of a fairly high interfacial resistance that is either causing the current to avoid the  $Bi_2Te_3$  altogether and go through the polymer film, or it goes through the  $Bi_2Te_3$ , but only after overcoming the resistance at the interface. These results provide valuable insight into the interactions



between P3HT and  $\text{Bi}_2\text{Te}_3$  that could be important to consider when designing composites of these two materials.

## CONCLUSION AND FUTURE WORK

By fabricating bilayer devices that contained pieces of  $\text{Bi}_2\text{Te}_3$  surrounded by P3HT film and calculating the resistive properties of the devices and materials, it was shown that some degree of interfacial resistance must exist between the two materials. The apparent resistivity of each material was used to show that this interface resistance was substantially high and accounted for about half of the total device resistance in devices with varying dopant concentrations. These results could prove useful in developing a model for compatibility between polymeric and inorganic material in conductive composite devices.

To develop a more complete and accurate model of the compatibility between  $\text{Bi}_2\text{Te}_3$  and P3HT, it would be useful to conduct this study with more controlled cutting of the  $\text{Bi}_2\text{Te}_3$  to ensure that the number of surface and internal defects in the material is reduced to the greatest degree possible. This would also allow for more consistency in the sizes of the  $\text{Bi}_2\text{Te}_3$  pieces. Doing so would provide the most accurate insight possible into the magnitude of the interfacial resistance. It would also be useful to gather data on the interface between  $\text{Bi}_2\text{Te}_3$  and other conductive polymers to see if similar results are found or if the compatibility between the metal and polymer varies substantially for other systems. This would provide a broader perspective on the electrical interactions between polymers and metals and would be essential in developing future models on their compatibility.

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## VITA

Evan “Kris” Kirksey was born in Richmond, Virginia in 1989. He lived there through high school and developed an early love for science and technology. In 2007, he began attending the University of Virginia, where he received a B.S. in Computer Engineering and a B.S. in Economics. He worked as a web developer for a couple years before deciding to pursue a career in a laboratory research setting and applying for the M.S.E. program in Materials Science and Engineering at Johns Hopkins University. In Professor Howard Katz’s lab, he was able to pursue his interest in renewable energy by studying thermoelectric materials and conductive polymer composites. After receiving his M.S.E., he plans to pursue a Ph.D. conducting research in the areas of energy capture and storage.



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